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Supplemental Response

Remarks

Reconsideration of pending Claims 1-73 and 101-129 is respectfully requested.

Claims 1, 11, 16, 22, 26, 30, 33, 46, 50, 52, 62, 66-73, 101-110, 112-114, 116-117, 119-124, and 127-129 have been amended. Claims 40 and 55 have been cancelled.

The claims have been amended to more clearly recite the features of forming the conductive contact. The claims as amended recite that the heat step (700°C or greater) is performed on a contact having a thickness of about 500 *angstroms or greater*, and results in a *reduction of chlorine¹* and a *contact without substantial cracks*.

Support for the amendments to the claims is in the specification at page 14, line 4 ("...particularly when the thickness of the contact reaches about 500 angstroms or greater...), at page 3, lines 21-23 ("...It has also been found that conducting a CMP process to remove excess material from the substrate prior to the anneal step avoids undesirable problems with cracking of the film layer and the wafer substrate....), page 6, lines 7-10 ("...The present method provides a process of removing undesirable components such as chlorine and the like, from a contact which overcomes problems in the art with cracking from anneal processing steps...), and page 14, lines 9-12 ("...In addition, conducting the thermal anneal step after removing excess conductive material from the surface of the substrate eliminates problems encountered with cracking of the film layer and/or the substrate with thermal anneals performed on a blanket material layer overlying the substrate.).

No new matter is added with these amendments to the claims, which are intended to merely clarify language used in the claims and/or the subject matter claimed. The scope of the claims is intended to be the same after the amendment as it was before the amendment.

Rejections under 35 U.S.C. § 103(a)

The Examiner maintains the rejection of Claims 1, 2, 3-9, 11-14, 16-19, 21-24, 26-28, 30, 31, 34, 35, 37, 38, 40-45, 49, 68, 71, 101-105, 112, 114, 116, 120, and 121 as obvious over Wang (US 2002/0155219) in view of Hu (USP 6,436,820). This rejection is respectfully traversed.

¹ Claim 1 recites "a component."

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Neither Wang nor Hu teach or suggest a method of forming a contact by a) depositing a titanium nitride (or titanium boronitride) layer to fill an opening, then b) removing excess material to form a contact within the opening which is at least about 500 Å thick, and then c) heat treating the contact with a nitrogen gas at 700°C or greater to decrease the amount of chlorine within the contact, wherein the contact has substantially no cracks.

Both Wang and Hu teach forming a TiN film layer of no more than 400 Å, and then heat treating the layer (at less than 700°C) to remove chlorine from the layer. Both Hu and Wang further disclose performing a *series of deposition/treatment steps* to provide a TiN layer having a combined desired thickness that is substantially free of cracks.

See Hu, for example, at col. 2, lines 30-39, and at col. 4, lines 49-54 (emphasis added):

...The method comprises forming a layer of TiN having a thickness of 400 Å or less by chemical vapor deposition...; and, repeating the film forming and halogen residue removal steps multiple times, to form a multi-layer TiN film having the desired thickness...The use of a series of deposition-anneal steps provides for a more complete removal of halogen residues from the thick titanium nitride film while permitting a rapid film deposition rate...

...In addition, Applicants discovered if a very thick film (1,000 Å or greater) is annealed in the presence of NH₃, the residual halogen atoms will cause the film to form micro cracks. However, applicants discovered that annealing can be carried out without causing such cracks to form if the thickness of the film being annealed does not exceed 400 Å.

Likewise, see Wang at the following paragraphs (emphasis added):

[0007] ...Thus, a TiN film may be formed by high temperature CVD using a reaction between TiCl₄ and ammonia (NH₃). However, thicker TiN films deposited using some prior art processes tend to develop cracks, especially when the film thickness exceeds about 400 Å. With increasing film thickness, both the density and size of the cracks increase, until the film eventually peels off.

...[0022] In one embodiment... The deposited TiN layer, having a thickness of up to about 300 Å, is then exposed to a hydrogen-containing plasma. The plasma-treated TiN layer has a reduced resistivity compared to the as-deposited TiN layer due to a lower Cl content.

...[0024] Depending on the specific application, the film deposition and plasma treatment steps can be repeated for additional cycles to yield a composite TiN layer. For example, a thick TiN layer can be obtained for thicknesses above 1000 Å.

...[0042] Depending on the deposition temperature and the NH₃:TiCl₄ ratio, the as-deposited TiN film may have a chlorine content as high as about 5%. In accordance with the present invention, the TiN layer 204 is subjected to a plasma treatment step, as illustrated in FIG. 2c. In

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particular, the TiN layer 204, e.g., having a thickness up to about 300 Å, is exposed to a hydrogen-containing plasma 210...

...
[0049] In general, a composite TiN layer of desired thickness may be formed from an aggregate of TiN component layers by repeating several cycles of film deposition and plasma treatment. Optimization of the deposition and plasma treatment conditions for individual TiN components layers will result in a composite TiN layer having the combined advantages of improved step coverage and reduced film stress.

Neither Wang or Hu teach or suggest Applicant's method of forming a contact by:

- filling an opening with TiN,
- then removing excess material from the structure to form a contact within the opening, which is at least about 500 Å thick, and
- then heat treating the contact to remove chlorine without forming substantial cracks within the contact.

Both references explicitly teach away from forming and heat-treating a layer that is more than 300 or 400 Å thick.

In contrast, with Applicant's methods as claimed, a TiN fill that is 500 Å or greater can be formed without substantial cracks and a low level of chlorine (or other component) without multiple deposition/heat treatment steps -- by depositing the TiN material to fill an opening, then removing excess material to form the contact within the opening, and then heat treating the TiN contact in a nitrogen gas (e.g., NH₃) at a temperature of about 700°C. or greater to remove the chlorine (or component) from the contact.

Applicant's method eliminates the need for conducting multiple depositions and heat treatments to form a contact greater than 400 Å as taught by both Wang and Hu.

In addition, Applicant reiterates that the Examiner has provided no sound reasoning to modify Wang's process temperature as proposed, other than hindsight — particularly with regard to the proposed increase of Wang's (and Hu's) temperature to 700 C. or greater. Although Applicant has provided arguments to the Examiner's proposed increase in temperature, the Examiner has failed to properly respond.

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The Examiner cites to Hu's NH₃ treatment at 680 C. as the basis for modifying Wang's 400-600 C hydrogen plasma treatment to a 700 C or greater NH₃ treatment step. However, this requires a) replacing Wang's 400-600 C temperature treatment with a 680 C. treatment (as taught by Hu), and then b) increasing Wang's 680 C temperature to 700 C.

The Examiner has combined the references using hindsight reasoning, taking Applicant's disclosure as a guide for piecing together the cited prior art— particularly for the proposed increase of Wang's (and Hu's) temperature to 700 C. or greater. Although Hu teaches the use of a 680 C. heat treatment, Hu provides no information that would motivate an art worker to further increase the heat treatment temperature. The Examiner has showed no good basis why a skilled artisan with no knowledge of the invention, would increase the heat treatment temperature to 700 C. or greater.

In sum, nothing in either Wang or Hu teaches or suggests Applicant's methods as claimed. Accordingly, withdrawal of this rejection is respectfully requested.

Rejections under 35 U.S.C. § 103(a) (Wang with Hu and Leem or JP '220)

The Examiner maintains the rejection of Claim 115 and Claims 10, 15, 20, 25, 29, 32, 39, 50-59, 61-63, 66, 67, 69, 70, 72, 73, 106-111,² 113, 117-119, 122, and 123 based on the combination of Wang and Hu with Leem (USP 6,284,646) or Japan '220 (JP 5267220). The Examiner maintains that Leem or Japan '220 provide motivation to incorporate boron into the TiN material of Wang or to form one or more of the titanium nitride layers of Wang using titanium boronitride. These rejections are respectfully traversed.

Neither Leem nor Japan '220 makes up for the deficiencies of the primary references of Wang and Hu to provide Applicant's methods as claimed.

The mere incorporation of boron into the TiN material of Wang would not achieve Applicant's method as claimed. As discussed above, neither Wang nor Hu teach or suggest Applicant's method of forming a contact by a) depositing a titanium nitride (or titanium boronitride) layer to fill an opening, then b) removing excess material to form a contact within the opening which is at least about 500 Å thick, and then c) heat treating the contact with a

² It is noted that Claim 109 does not recite a boron-containing material.

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nitrogen gas at 700°C or greater to decrease the amount of chlorine within the contact, wherein the contact has substantially no cracks.

Nor do the disclosures of Leem and Japan '220 provide any information on *filling an opening* with titanium boronitride material to a thickness of at least about 500 Å, or any subsequent heat treatment to remove chlorine from the contact.

Leem discloses the use of titanium boronitride to form *thin buffer layers* (26, 30, 34) — each having a thickness of *100 Å or less* — between alternating metal layers (24, 32, 36). See at col. 6, line 45 to col. 7, line 22 (emphasis added), and FIG. 2C below:

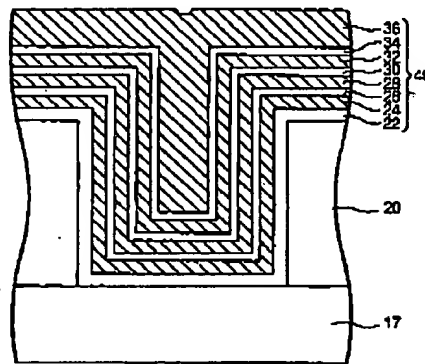


FIG. 2C

A buffer layer 26 having a *thickness of approximately 100 Angstroms or less* is formed on the first conductive layer 24. The buffer layer 26 is preferably a layer of a material having no significant effect on electrical characteristics of the composite layer including layers 24 and 26 and other conductive layers formed subsequently thereon. ...the buffer layer 26 can be a layer of a material such as ...titanium boron nitride (Ti-B-N)...

A second conductive layer 28, such as an aluminum layer, is formed on the buffer layer 26...

Additional conductive layers 32 and 36 and *alternating buffer layers 30 and 34* can be formed repeatedly using the methods discussed above to provide a smooth and planar composite (or laminated) conductive layer of a desired thickness. In particular, each of the subsequent conductive layers is formed on a respective buffer layer, and the formation of each conductive layer is terminated when a reflective index thereof reaches a predetermined value. More particularly, each conductive layer preferably has a thickness in the range of approximately 500 Angstroms to 1500 Angstroms, *and each of the buffer layers preferably has a thickness of less than approximately 100 Angstroms* so that the overall thickness of the completed composite conductive layer can be determined by the number of conductive and buffer layers thus formed.

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Likewise, Japan '220 discloses the use of $\text{TiB}_x\text{N}_{1-x}$ to form an *adhesion layer (110)* between a titanium (Ti) barrier layer (108) and a metal plug (112) that fills the opening (106).

See Example 5 at [0046]-[0051], and FIG. 1(C):

[0046] (Example 5) An example 5 is an example which applied the adhesion layer of this invention, and the metal plug formation method when a contact hole was formed by blanket tungsten CVD, forms Ti layer first between a semiconductor substrate and the metal layer which consists of a tungsten, and subsequently forms $\text{TiB}_x\text{N}_{1-x}$ in it as an adhesion layer...

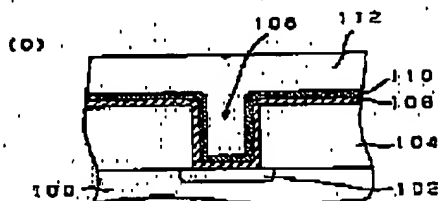


FIG.1(C)

[106 = opening; 108 = Ti layer; 110 = $\text{TiB}_x\text{N}_{1-x}$ layer; 112 = metal plug]

Neither Leem nor Japan '220 teach or suggest the use of titanium boronitride to fill an opening to form a contact. The titanium boronitride layers (26, 30, 34) of Leem and the $\text{TiB}_x\text{N}_{1-x}$ adhesion layer (110) of Japan '220 are not formed as fills within an opening and do not form contacts or plugs. Rather, *tungsten* fills the opening (106) in Japan '220 to form the plug (112). In Leem, alternating *metal layers* (24, 32, 36) and buffer layers (26, 30, 34) form the fill.

Both Leem and Japan '220 teach forming a titanium boronitride layer between two metal layers – in Leem, between Al layers (24, 32, 36), and in Japan '220, between Ti layer (108) and the tungsten plug (112) that fills the opening (106).

There is nothing in either Leem or Japan '220 that provides any information on titanium boronitride to fill a contact opening to form a conductive contact. The teachings of these references are limited to the formation of titanium boronitride *as a layer between two metal layers* within a contact opening — *not* as a fill material.

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Nor do Leem or Japan '220 teach the formation of a contact having *the amounts of boron and nitrogen* and mechanical properties that are recited in Claims 59 (below), and 66, 67, 70, and 117-118:

...having an amount of boron to substantially eliminate peeling of the contact from the sidewall of the opening and cracking of the insulative layer, and an amount of nitrogen to provide an effective amount of conductivity to an active area within the substrate.

As discussed by Applicant in the specification (at pages 2-3), the boron-doped titanium nitride fills of the invention overcome problems posed by pure TiCl_4 -based TiN fills. Applicant's boron-doped TiN fills are formulated with an amount of boron and nitrogen to provide a high level of adhesion to insulative sidewalls of the contact opening to eliminate peeling of the contact from the sidewalls and cracking of the insulative layer, and an effective conductivity level.

The present TiCl_4 based titanium nitride films...also overcome inadequacies of pure TiCl_4 based titanium nitride films that are used as fill material for forming conductive contacts or interconnects within contact openings formed through an insulative layer of a semiconductor structure. Pure TiCl_4 based titanium nitride fills do not adhere well to the surface of insulative sidewalls of a contact opening, and can also cause the insulative layer to crack due, at least in part, to the pressure exerted when the thickness of the fill within the contact opening is about 200 angstroms or greater.

The present invention overcomes the problems of a pure TiCl_4 based titanium nitride plugs or barrier film by incorporating diborane (B_2H_6) into the gas mixture to dope the TiCl_4 based titanium nitride film during the deposition process. The addition of B_2H_6 to the precursor gas used to form the TiCl_4 based titanium nitride film has been found to improve the mechanical properties of the resulting titanium nitride film with substantially no impact on its conductive properties. In particular, the gaseous mixture used to form the boron-doped, titanium nitride contacts comprises diborane (B_2H_6) in an amount effective to provide a contact having an amount of boron to provide a level of adhesion of the conductive contact to the insulative sidewalls of the contact opening to substantially eliminate peeling of the contact from the sidewalls and cracking of the body of the insulative layer. The mixture further includes an amount of ammonia (NH_3) to provide the contact with a level of nitrogen effective to maintain the conductivity of the contact at a predetermined level for an effective electrical contact with a conductive or active area within the substrate to/from an active area within a semiconductor device and/or a memory or logic array.

Additionally, Applicant found that, when subjected to the heat treatment step according to Applicant's method to remove chlorine from the contact, *the boron-doped TiN contacts retain the foregoing properties*. See the specification at pages 11-12 (emphasis added):

Advantageously, the present process of first removing the excess contact material by CMP, and then thermally annealing the titanium nitride fill material remaining as the contact 34 in a

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nitrogen containing gas such as ammonia, *reduces the chlorine content in the fill material without significantly changing the other properties of the film stack, particularly the advantages provided by the incorporation of boron into the film layer.*

...Boron doped titanium nitride contacts also possess a high level of adhesion to the insulative sidewalls of the opening, have a sufficiently low thermal stress level, measured in force per unit area (i.e., Gdynes/cm²), to substantially eliminate cracking of the insulative layer, and are highly conductive with low electrical resistivity.

Leem and Japan '220 provide no information on *filling a contact opening* with boron-doped TiN, or the *effective amounts of boron and nitrogen* to eliminate peeling of the contact and cracking of the adjacent insulative layer (caused by pressure exerted when an opening is filled with a TiN fill of 200 Å or greater), and to maintain a suitable level of conductivity within the contact. Both references describe forming a buffer or adhesion layer between metal layers that form a fill an opening.

Nor do Leem or Japan '220 provide any information on a heat treatment of a titanium boronitride material that fills a contact opening — or whether the properties of adhesion, low thermal stress, and low resistivity of the titanium boronitride fill are maintained following a heat treatment at 700°C or greater to remove the chlorine component from the contact.

Moreover, none of the cited references teach or suggest forming *alternating layers of TiN and boron-doped TiN* to fill a contact opening as recited in Claims 61-63, 67 (below), 69, 70, 73, 106-108, and 119:

...forming a titanium nitride layer over the titanium silicide by depositing a layer of titanium nitride over the titanium silicide layer; and sequentially depositing overlying layers of boron-doped titanium nitride and titanium nitride to fill the opening, wherein the boron-doped titanium nitride layer is interposed between two titanium nitride layers;

Japan '220 teaches a *single* layer (110) of TiB_xN_{1-x} between a Ti layer (108) and a metal fill (112). Leem teaches buffer layers (26, 30, 34) at 100 Å or less — positioned between aluminum layers (24, 32, 36).

The advantages of a conductive contact formed from alternating layers of TiN and boron-doped TiN, and treated to remove chlorine from the contact, are discussed in the specification at pages 13-14:

Sandwiching a layer of boron-doped titanium nitride 32' between undoped titanium nitride substantially reduces the thermal stress in a TiCl₄-based TiN fill material. ...The combination of alternating layers achieves a TiCl₄-based TiN contact having a level of adhesion that substantially eliminates peeling of the formed contact from the sidewalls of the contact opening.

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It also provides a lowered level of thermal stress that substantially reduces cracking of the body of the insulative layer, particularly when the thickness of the contact reaches about 500 angstroms or greater. In addition, the resulting contact has a high level of conductivity for an effective electrical contact to a diffusion region or other conductive structure...

None of the cited references teach or suggest filling a contact opening with alternating layers of TiN and boron-doped TiN — or a fill having an effective level of adhesion to eliminate peeling of the contact and cracking of the adjacent insulative layer, and an effective level of conductivity — which mechanical properties are maintained following a heat treatment at 700°C or greater to remove the chlorine component from the contact.

Regarding Claims 56 and 111, it is further noted that these claims recite forming and heat treating a contact that is about *1000-3000 angstroms thick*. As discussed above, neither Hu nor Wang teach or suggest heat treating a fill having a thickness greater than 400 Å thick.

In sum, the combination of Wang and/or Hu with either Japan '220 or Leeds would not provide Applicant's methods as claimed. Accordingly, withdrawal of these rejections is respectfully requested.

Rejections under 35 U.S.C. § 103(a) (Wang with Hu, and Doan)

The Examiner maintained the rejection of Claims 36, 46, 47, 48, 64 and 65 based on the combination of Wang and Hu with Doan (US 2001/0006240). The Examiner cites to Doan for motivation to form a titanium silicide (TiSi₂) layer by PECVD or sputtering. This rejection is respectfully traversed.

The mere formation of a TiSi₂ layer in the TiN film construction of Wang does not make does not make up for the above-stated deficiencies in the rejection of the claims based on the Examiner's combination of Wang with Hu. As discussed above, neither Wang nor Hu teach or suggest Applicant's method of forming a contact by a) depositing a titanium nitride (or titanium boronitride) layer *to fill an opening*, then b) *removing excess material* to form a contact within the opening which is *at least about 500 Å thick*, and then c) *heat treating* the contact with a

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nitrogen gas at 700°C or greater to decrease the amount of chlorine within the contact, wherein the contact has substantially no cracks.

The combination of Doan with Wang and Hu does not teach or suggest Applicant's methods as claimed. Accordingly, withdrawal of this rejection is respectfully requested.

Rejections under 35 U.S.C. § 103(a) (Wang with Hu, with AAPA)

The Examiner rejected Claims 60 and 124, 125, 126, and 127 based on the combination of Wang and Hu in view of "applicant's admitted prior art (AAPA)". The Examiner maintains that it would be obvious to combine Wang's disclosure of forming a contact to a source/drain with the purported AAPA of forming aluminum interconnects over contacts to form a source/drain contact and/or an interconnect. This rejection is respectfully traversed.

The mere formation of the contact to an S/D region in the substrate or the formation of an interconnect over the titanium nitride film of Wang do not make up for the above-stated deficiencies in the rejection of the claims based on the Examiner's combination of Wang with Hu.

The combination of AAPA with Wang and Hu does not teach or suggest Applicant's methods as claimed. Accordingly, withdrawal of this rejection is respectfully requested.

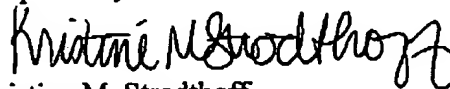
Extension of Term. The proceedings herein are for a patent application and the provisions of 37 CFR § 1.136 apply. Applicant believes that no extension of term is required. However, this conditional petition is being made to provide for the possibility that Applicant has inadvertently overlooked the need for a petition for extension of time. If any extension and/or fee are required, please charge Account No. 23-2053.

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Based on the above remarks, the Examiner is respectfully requested to reconsider and withdraw the rejections of the claims. It is submitted that the present claims are in condition for allowance, and notification to that effect is respectfully requested.

Respectfully submitted,



Kristine M. Strodthoff
Reg. No. 34,259

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WHYTE HIRSCHBOECK DUDEK S.C.
555 East Wells Street
Suite 1900
Milwaukee, Wisconsin 53202-3819
(414) 273-2100

Customer No. 31870